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TEXT-BOOKS OF PHYSICAL CHEMISTRY

Edited by Sir WILLIAM RAMSAY, K.C.B., F.R.S.

A SYSTEM OF PHYSICAL CHEMISTRY

T

Systems in Equilibrium.

Static Equilibrium.
(Treated in "Mechanics.")

Dynamic Equilibrium.

Physical, i.e. Distribution of Molecules in space. States of matter. Continuity of liquid and gaseous states. Constitution of solids. Applications of the Unitary Theory of Energy.

Chemical Equilibrium in Homogeneous Systems, or "*Homogeneous Equilibrium.*"

Homogeneous Equilibrium, effects due to Gravitation or Radiant Energy being absent. Law of Mass Action.

Homogeneous Eq
um affected by
Energy. Photo
"Equilibrium" ar
chemical " St
State."

Homogeneous Equilibrium in Gaseous Systems:
(*a*) Reactions involving no change in the number of molecules.
(*b*) Reactions involving change in the number of molecules.

Homogeneous Equilibrium in Liquid Systems:
(*a*) Liquid mixtures.
(*b*) Dilute solutions. (Osmotic pressure. Electrolytic dissociation. Osmotic theory of electromotive force.)
(*c*) Concentrated solutions.

Homogeneous Equilibrium in Solid Systems: Solid Solutions.

A SYSTEM OF
PHYSICAL CHEMISTRY

IN TWO VOLUMES

BY

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WITH DIAGRAMS

VOLUME I

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B

"SCIENCE is nothing without generalizations. . . . The suggestion of a new idea, or the detection of a law, supersedes much that had previously been a burden upon the memory, and by introducing order and coherence facilitates the retention of the remainder in an available form."

LORD RAYLEIGH.

information I am indebted to the Secretary of the Committee, Professor Alexander Findlay.

I would also take this opportunity of expressing my warmest thanks for the assistance which I have received on various occasions from my colleagues and friends, Professor F. G. Donnan, F.R.S., University College, London; Professor A. W. Porter, F.R.S., University College, London; Professor N. T. M. Wilsmore, University of Western Australia, Perth; and Professor W. B. Morton, Queen's University, Belfast.

various portions, each of which may rotate or vibrate with respect to one another, the number of degrees of freedom of the body is correspondingly increased, and to estimate the actual number of degrees of freedom soon becomes impossible. The important generalisation connected with degrees of freedom, and known as Boltzmann's " theorem of the equipartition of energy" between the different degrees of freedom possessed by a body may be stated thus: The total kinetic energy of a system (due to translation, rotation, vibration, etc.) is *equally* divided up between all the degrees of freedom, and it can be shown that the amount of energy per degree of freedom amounts to $\frac{1}{2}RT$, the unit of mass being the gram-mole. This theorem has been much criticised, but it would be altogether beyond our purpose to attempt to follow it. The application of the theorem in connection with the heat content of solids is discussed in Part III. (Vol. II.).

Although we have not been able to infer much regarding constitution from specific heat, a more successful attack has been made upon the problem from the standpoint of "electrons" or "corpuscles," of which, according to Sir J. J. Thomson, electricity—negative electricity—itself consists.

§ 4

Some Applications of the Corpuscular or Electron Theory to the Problem of Molecular and Atomic Constitution.

According to this theory, negative electricity consists of extremely small particles called corpuscles or electrons, which are all identical in size, and carry the same charge. These corpuscles are much smaller than atoms, and according to the theory, atoms, and therefore molecules, are partly built up of corpuscles. Of course to prevent spontaneous disintegration of the atom due to the mutual repulsion of a number of similarly charged electrons, it is necessary to assume the existence of an equal amount of positive electricity. It is assumed, therefore, that a neutral atom consists of a sphere of positive electricity (J. J. Thomson) which contains a number of corpuscles moving in various orbits, the number of such corpuscles and the kind of motion they possess being the ultimate source of chemical and physical "properties." It will be of interest to consider briefly the experimental evidence in favour of the real existence of corpuscles.

Corpuscles were first discovered during the electrical discharge through a highly exhausted tube. Rays are shot off from the cathode, and these may be stopped by the interposition of some material placed in their path. These cathode rays, as they are called, on striking the walls of the tube cause a vivid green fluorescence upon soda glass, blue on potash glass. That these rays consist of negatively charged particles was shown by the fact that they can be deflected in certain directions by a magnetic or an electrostatic field, or both simultaneously. The first important quantity which would serve to characterise these rays is the ratio of their mass to their charge. To obtain this we have to consider the effects produced by a magnetic and an electrostatic field upon the direction of motion of the particles. Suppose that a single corpuscle mass m carrying a charge e is moving with a velocity v cms. per second through the tube, then by putting on a magnetic field of strength H it is possible to deflect the course of the corpuscle in a given direction. If simultaneously an electrostatic field be set up (by connecting two parallel pieces of metal placed inside the tube to the two ends of a battery) in such a direction that it just compensates the effect of the magnetic field so that the path of the corpuscle is undeflected, than we can equate the effect due to the magnetic field to that due to the electrostatic. The magnetic force acting amounts to Hev, and if X is the strength of the electrostatic field the electrostatic force exerted upon the electron is Xe, so that when these two forces just balance we have—

$$Hev = Xe$$

or

$$v = \frac{X}{H}$$

By means o this equation one can determine the velocity of

t° centigrade.	Density of liquid.	Density of saturated vapour.	Pressure exerted by system.
0	0·914	0·096	34·3 atmos.
5	0·888	0·114	39·0 ,,
10	0·856	0·133	44·2 ,,
15	0·814	0·158	50·0 ,,
20	0·766	0·190	56·3 ,,
25	0·703	0·240	63·3 ,,
28	0·653	0·282	67·7 ,,
29	0·630	0·303	69·2 ,,
30	0·598	0·334	70·7 ,,
30·5	0·574	0·356	71·5 ,,
31	0·536	0·392	72·3 ,,
31·25	0·497	0·422	72·8 ,,
31·35	0·464	0·464	72·9 ,,

Hence critical temperature = 31·35° C.; critical pressure = 72·9 atmospheres; critical volume = $\frac{1}{0{\cdot}464}$ c.c.

If the values of the densities of liquid and vapour are plotted against temperature, one obtains a closed curve of the shape shown in Fig. 16.

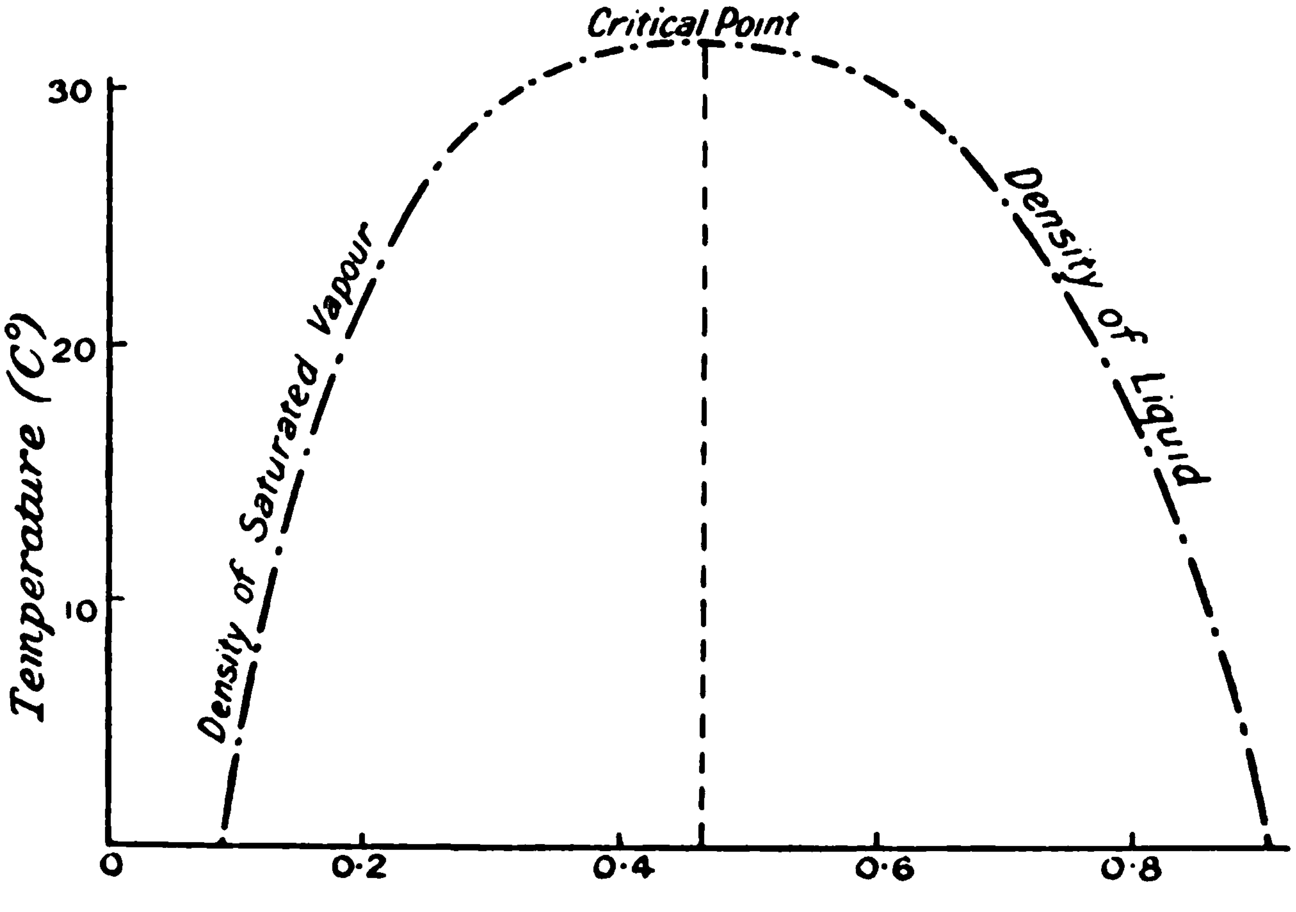


FIG. 16.

If the *mean* value of the density of liquid and density of vapour at each temperature be likewise plotted, it will be found

behaviour may be observed in the case of the system when entirely gaseous, which decreases in volume as the pressure increases, so that the line HC is followed. On reaching C the system usually becomes partly liquid, that is, partial condensation occurs, the system now following the line CA. Under certain conditions, however, *e.g.* in the absence of condensation nuclei, the system remains gaseous, even on being compressed beyond C, so that the line HC continues unbroken to some point such as D, when in general sudden (partial) condensation occurs and the pressure and volume of the system corresponds to some point on CA.

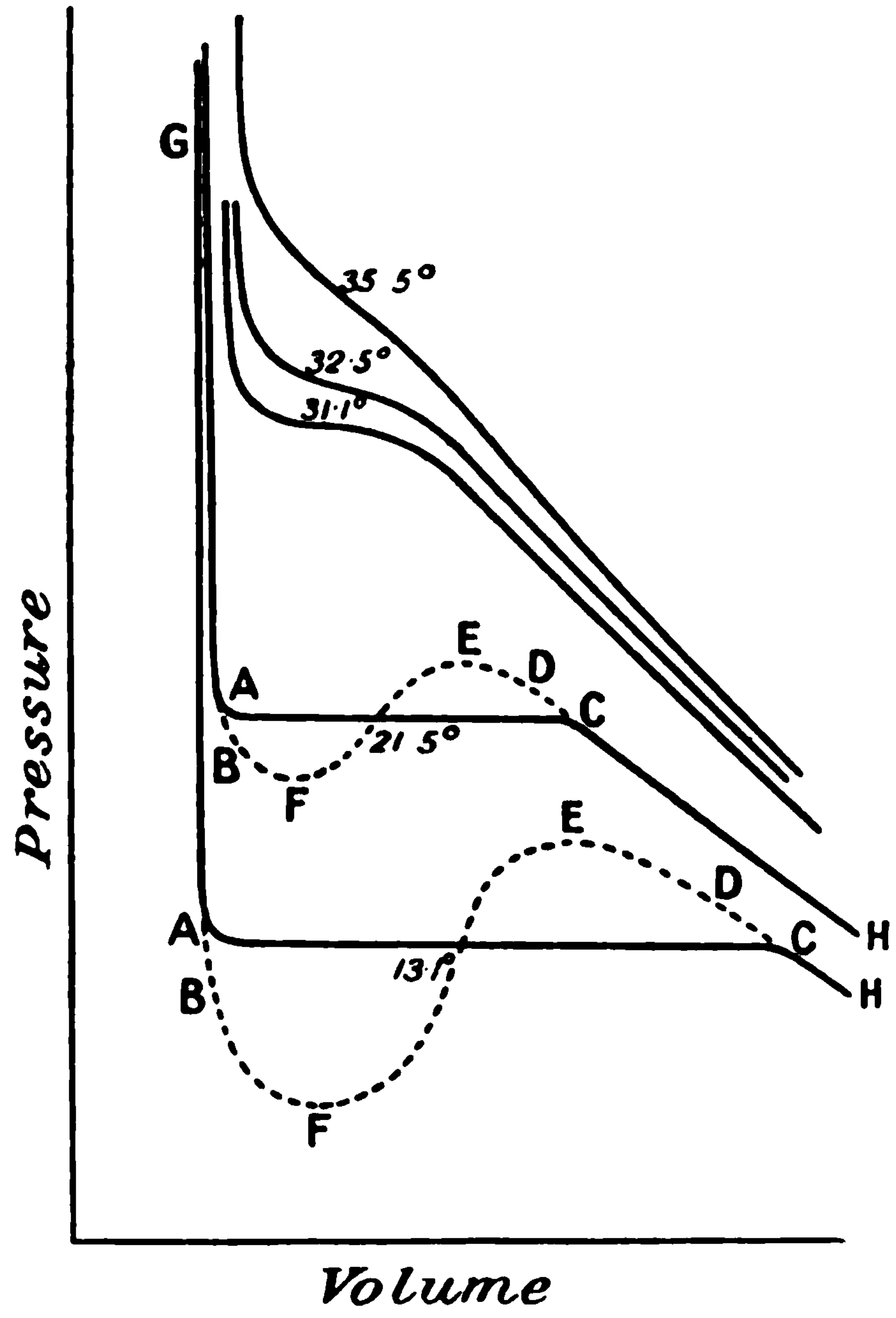


FIG. 18.

The dotted lines indicate on this CO_2 diagram Thomson's hypothetical isothermals.

Thomson considered that this idea of continuity might be

volumes the values decrease. At still greater volumes they appear to be constant."

The general conclusion is that the Ramsay and Young equation is very nearly but not quite in agreement with the actual behaviour of liquid and gas systems.

II. The Equation of van der Waals[1]

This expression is wider in its scope than the first-quoted form of the Ramsay and Young equation, in that it is proposed as a substitute for the entire "perfect gas" law $pv = RT$, and is to be applicable to actual gases and liquids.

It is written thus—

$$\left(p - \frac{a}{v^2}\right)(v - b) = RT$$

Where a and b are regarded as constants characteristic of a given substance, but independent of temperature and volume. p, v, R, T, have their usual significance. The above expression differs from the perfect gas law in that it contains two correction terms, $\frac{a}{v^2}$ and b. The term $\frac{a}{v^2}$ is introduced to take account of the attractive forces between the molecules.[2] These forces are extremely great when the system is liquid, and although decreasing rapidly with temperature rise and rarefaction, are still not negligible until the system is well above the critical point. The perfect gas law $pv = RT$ assumes, of course, that there are no such *cohesive* forces operating between the molecules. In the interior of actual gases, vapours, and liquids, the cohesive forces which exist, say, upon a single molecule are mutually destructive because they are on the average exerted in all directions

---

[1] J. D. van der Waals, *Dissertation*, Leyden, 1873; *Die Continuität des gasförmigen und flüssigen Zustandes*, Teile I. u. II., Leipzig, 1899. There is also an English translation of the German edition of 1881 in the *Physical Society Memoirs*.

[2] It will be remembered that in the introductory chapter it has been shown that the van der Waals' equation assumes the law of attraction to be the inverse fourth power of the distance between the molecules.

$(v - b)$, and this is the quantity which should appear in any modified form of Boyle's Law, for this law does not take account of any volume occupied by the molecules themselves. [It is more than likely that the law governing the actual compressibility of the molecules themselves is entirely different from a simple one such as that of Boyle.] When we allow, therefore, for the simultaneous modification of the pressure and volume terms, the corrected expression, put in the shape of a "Boyle's Law," takes the form—

$$\left(p + \frac{a}{v^2}\right)(v - b) = k$$

Now, if we simply make the *assumption* that the terms $\left(p + \frac{a}{v^2}\right)$ and $(v - b)$ should replace p and v in the general gas equation, we obtain—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

The above deduction of van der Waals' equation serves only to show the reasonableness of the modifications introduced. Van der Waals himself followed a more rigid method, starting from the Clausius virial.[1]

Van der Waals' expression is a cubic equation in v, as is seen when it is rewritten in the form—

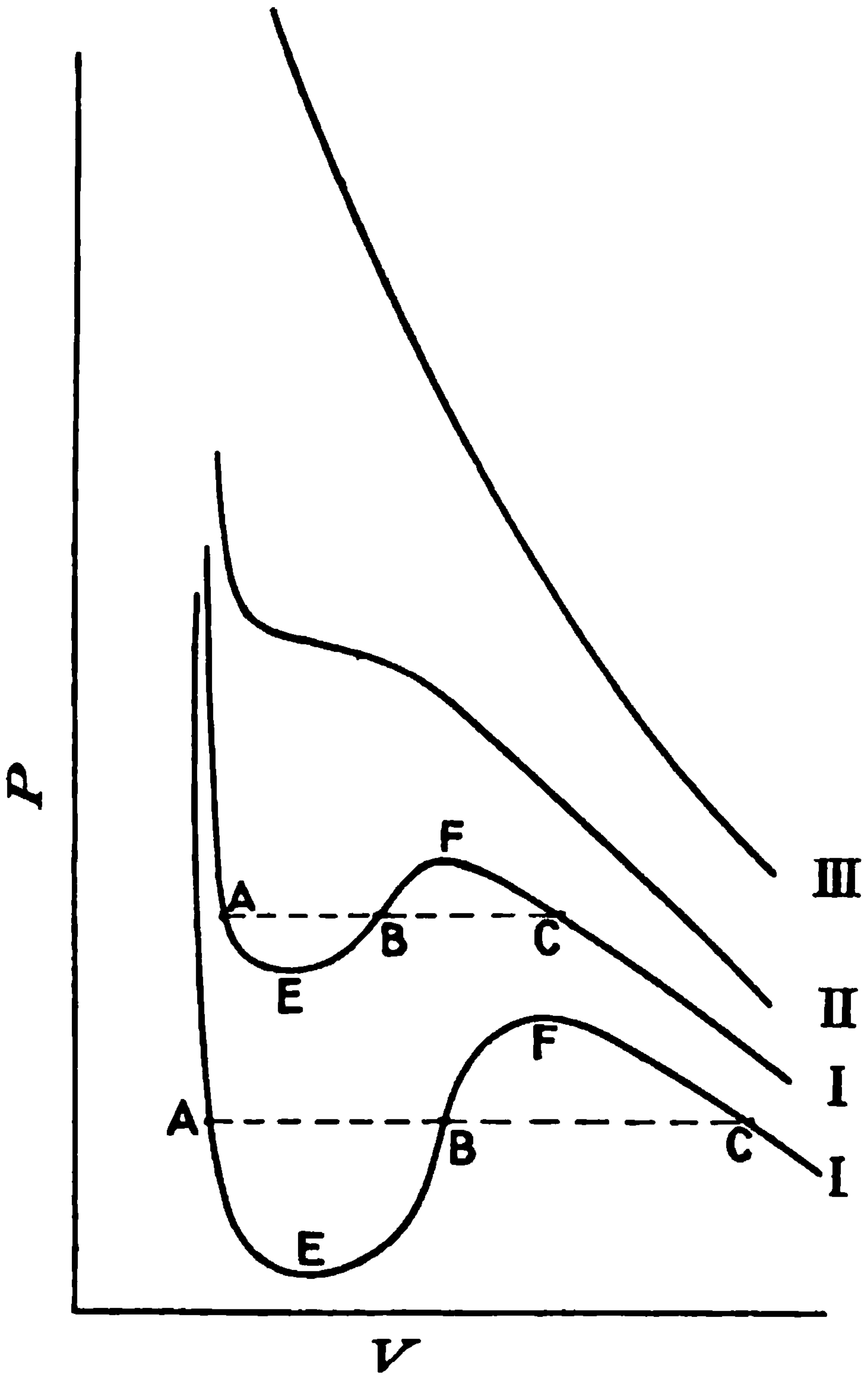
$$v^3 - \left(b + \frac{\mathrm{RT}}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0$$

The equation has therefore three roots, *i.e.* three values of v for any given p and T, and further, all three roots may be real, or one real and two imaginary. The expression is therefore the equation of curves such as those shown in the diagram, Fig. 20.

When the roots are real and different, three different values for v (for a given p and T) are shown by the points A, B, and C in curve I on the pv diagram. When the p and T values are such that the three roots are real and identical, the curve given by the equation is represented by II. When there is one real root and two imaginary, the curve has the shape represented

---

[1] The reader should consult van der Waals' monograph or Kuenen's *Die Zustandsgleichung*, in the "Wissenschaft" series.



VAN DER WAALS ISOTHERMALS.

FIG. 20.

by III. The resemblance between these curves and those suggested by James Thomson for the isothermals below, at, and above the critical point is very striking. The van der Waals equation carries out therefore this conception of the continuity of the liquid and gaseous states. It may also be pointed out that the equation predicts a similar continuity for

The equation of Dieterici may be put in a somewhat different and at the same time more general form if the term T be raised to the *n*th power, *n* being characteristic of the substance under investigation. The expression is then—

$$p = \frac{RT}{v-b} e^{-\frac{a}{T^n v}} .$$

By differentiation it follows that—

$$\frac{\partial \log p}{\partial v} = \frac{1}{p}\frac{\partial p}{\partial v} = -\frac{1}{v-b} + \frac{a}{T^n v^2}$$

and $$\frac{\partial}{\partial v}\left(\frac{\partial \log p}{\partial v}\right) = \frac{1}{p}\frac{\partial^2 p}{\partial v^2} - \frac{1}{p^2}\left(\frac{\partial p}{\partial v}\right)^2 = \frac{1}{(v-b)^2} - \frac{2a}{T^n v^3}$$

At the critical point each of these expressions is zero; that is—

$$\frac{1}{v_c - b} = \frac{a}{T_c^n v_c^2} \quad \text{and} \quad \frac{1}{(v_c - b)^2} = \frac{2a}{T_c^n v_c^3}$$

Whence $$v_c = 2b$$

$$T_c^n = \frac{a}{b4}$$

$$p_c = \frac{R\left(\frac{a}{4b}\right)^{\frac{1}{n}} . e^{-2}}{b}$$

and $$\frac{RT_c}{p_c v_c} = \frac{(v_c - b)}{v_c} e^2 = \frac{1}{2} e^2 = 3{\cdot}69 \text{ as before.}$$

The Variation of pv with p from the Standpoint of the General Dieterici Equation.

The general Dieterici equation yields the following expression for pv :—

$$pv = \frac{RTv}{v-b} e^{\frac{-a}{T^n v}}$$

Hence $$\log (pv) = \log RT + \log v - \log (v-b) - \frac{a}{T^n v}$$

or $$\frac{1}{pv}\frac{\partial (pv)}{\partial p} = \left(\frac{1}{v} - \frac{1}{v-b} + \frac{a}{T^n v^2}\right)\frac{\partial v}{\partial p}$$

some doubt on the numerical values of the degree of polymerisation obtained by the above means, some authors considering that the estimates of Ramsay and Shields are too high, others that polymerisation is a much more general phenomenon and that possibly even normal liquids are not quite free from it. The whole problem is only very partially solved.

The formation and decomposition of hydrobromic acid and hydrochloric acid—

$$2HBr \rightleftarrows H_2 + Br_2$$

(Bodenstein and Geiger, *Zeitsch. phys. Chem.*, **49**, 70, 1904);

$$2HCl \rightleftarrows H_2 + Cl_2$$

(Dolezalek, *Zeitsch. phys. Chem.*, **26**, 334, 1898).

Also the technically important reactions, namely, that dealing with the fixation of nitrogen from the air—

$$N_2 + O_2 \rightleftarrows 2NO$$

(Nernst, *Göttingen Nachrichten*, p. 261, 1904; Nernst, Jellinek, and Finckh, *Zeitsch. anorg. Chem.*, **45**, 116, 1905; **49**, 212, 1906; **49**, 229, 1906);

and the well-known water gas[1] equilibrium—

$$CO_2 + H_2 \rightleftarrows H_2O + CO$$

For details of these reactions the reader is referred to Haber's *Thermodynamics of Technical Gas Reactions.*

As already pointed out, a consequence of the absence of volume change in the above cases is that for all such reactions the numerical value of the equilibrium constant is the same, whether we express the active mass of the components either in concentration terms (gram molecules per liter) or in partial pressure terms (atmospheres). This can be seen at once by inspection of the equilibrium mass action equation, because the proportionality factor k connecting partial pressure with concentration occurs as often in the numerator as in the denominator, and therefore vanishes. On the other hand, suppose one considers a reaction in which there is a change in the total number of molecules as the reaction proceeds, thereby causing a change in volume (if the external pressure be kept constant), the numerical value of K will not be the same when expressed in concentration and partial pressure terms respectively. Thus, take the case of the decomposition of nitrogen peroxide—

$$N_2O_4 \rightleftarrows 2NO_2$$

---

[1] "Water gas" itself is produced by passing steam over heated carbon, thereby forming a mixture of CO_2, CO, H_2, and H_2O vapour. This mixture can be used as a gaseous fuel, since it gives out considerable heat when burnt with air.

the cation and anion respectively, and denoted them by U and V, *i.e.* $\Lambda_\infty = U + V$. He based this relationship on the purely additive character of the equivalent conductivities which he observed.[1]

His law means that the mobility of $Na^\cdot$, for example, should have the same value whether derived from chlorides or nitrates, etc. He verified it by showing that the following held true:—

$$\{\Lambda_\infty NaCl - \Lambda_\infty KCl\} = \{\Lambda_\infty NaNO_3 - \Lambda_\infty KNO_3\}.$$

We see that the law is in agreement with this experimental fact, because—

$$\begin{aligned}\Lambda_\infty NaCl &= U_{Na^\cdot} + V_{Cl'}\\ \Lambda_\infty KCl &= U_{K^\cdot} + V_{Cl'}\\ \Lambda_\infty NaNO_3 &= U_{Na^\cdot} + V_{NO'_3}\\ \Lambda_\infty KNO_3 &= U_{K^\cdot} + V_{NO'_3}\end{aligned}$$

and therefore

$$\begin{aligned}\Lambda_\infty NaCl - \Lambda_\infty KCl &= U_{Na^\cdot} + V_{Cl'} - U_{K^\cdot} - V_{Cl'} = U_{Na^\cdot} - U_{K^\cdot}\\ \Lambda_\infty NaNO_3 - \Lambda_\infty KNO_3 &= U_{Na^\cdot} + V_{NO'_3} - U_{K^\cdot} - V_{NO'_3}\\ &= U_{Na^\cdot} - U_{K^\cdot}\end{aligned}$$

The following numerical data are taken from the extended list given by Kohlrausch (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*). The value of Λ_∞ was found to have reached its limit when the concentration of solute was $\frac{N}{1000}$.

Salt.	Λ_∞	Therefore, assuming Kohlrausch's Law to be true—
KCl . . .	120·1	$U_{K^\cdot} - U_{Na^\cdot} = 21·0$
$NaCl$ . .	108·1	
KNO_3 . .	125·5	,, $= 20·9$
$NaNO_3$ . .	104·6	
KIO_3 . .	97·6	,, $= 20·9$
$NaIO_3$ . .	76·7	
$\frac{1}{2}K_2SO_4$ . .	133·5	,, $= 23·0$
$\frac{1}{2}Na_2SO_4$.	110·5	

The constancy of $(U_{K^\cdot} - U_{Na^\cdot})$ is borne out by these

---

[1] For a discussion of the mechanical friction of the solvent see a paper by Kohlrausch, *Proc. Roy. Soc.*, 71, 338, 1903.

v.	Λ.	α.	100 × α, *i.e.* the number of moles dissociated per 100 moles in solution.
1	69·5	0·675	67·5
2	75·7	0·736	73·6
10	86·5	0·841	84·1
20	89·7	0·872	87·2
100	96·2	0·935	93·5
500	99·8	0·970	97·0
1,000	100·8	0·980	98·0
5,000	101·8	0·989	98·9
10,000	102·9	practically unity, *i.e.* complete dissociation.	100
50,000	102·8 = Λ_∞		
100,000	102·4		

Similarly, for NH_4Cl, at the same temperature :—

v.	Λ.	α = dissociated fraction of one mole of solute.
1	90·7	0·750
2	94·8	0·784
10	103·5	0·856
20	107·8	0·892
100	114·2	0·945
500	118·0	0·976
1,000	119·0	0·985
5,000	120·4	practically unity
10,000	120·9 = Λ_∞	
50,000	120·9	

SILVER NITRATE, AT 25° C.

v.	Λ.	α.
16	102·25	0·828
32	108·00	0·874
64	111·02	0·899
128	114·34	0·926
256	116·87	0·947
512	118·75	0·962
	Λ_∞ = 123·45	

Reference may also be made to later papers upon the same subject (Ostwald, *Zeitsch. physik. Chem.*, **3**, 170, 241, 369 1889; Bredig, *ibid.*, **13**, 289, 1894). A few typical illustrations may be given.

PROPIONIC ACID, AT 25° C.

v liters.	Λ.	100 α.	K.
8	3·65	1·016	$0{\cdot}0_4130$
16	5·21	1·452	$0{\cdot}0_4134$
32	7·36	2·050	$0{\cdot}0_4134$
64	10·39	2·895	$0{\cdot}0_4135$
128	14·50	4·04	$0{\cdot}0_4133$
256	20·38	5·68	$0{\cdot}0_4133$
512	28·21	7·86	$0{\cdot}0_4131$
1024	38·73	10·79	$0{\cdot}0_4128$
	$\Lambda_\infty = 359$		Mean $0{\cdot}0_4134$

SUCCINIC ACID, AT 25° C.

v.	Λ.[1]	100 α.	K.
16	11·40	3·20	$0{\cdot}0_4662$
32	16·03	4·50	$0{\cdot}0_4662$
64	22·47	6·32	$0{\cdot}0_4667$
128	31·28	8·80	$0{\cdot}0_4664$
256	43·50	12·24	$0{\cdot}0_4668$
512	59·51	16·75	$0{\cdot}0_4659$
1024	81·64	22·95	$0{\cdot}0_4668$
2048	109·5	30·82	$0{\cdot}0_4671$
	$\Lambda_\infty = 355$		Mean $0{\cdot}0_4665$

Ostwald succeeded in confirming the dilution law for 250 acids. These were all weak acids. Similarly, Bredig found the law applicable in the case of 50 bases investigated by him.

---

[1] Succinic acid only splits off one $H^{\cdot}$ until great dilution is reached, *i.e.* it acts as a monobasic acid. The conductivity values are actually molecular conductivity, which is identical in this case with equivalent conductivity.

the equilibria relations of electrolytes in aqueous solution is that all (or nearly all) strong electrolytes—throughout the range of dilution 10–1000 litres—do not even approximately obey the dilution law. A few appear to do so, at least over a certain range of dilution, notably, amongst acids, dichloracetic acid, cyanacetic acid, and maleic acid, but these instances are relatively few in number.[1] All the ordinary inorganic salts (with the exception of cadmium and mercury (*ic*), halides, mercuric cyanide, and one or two ferric salts), all the ordinary inorganic acids and bases (with the exception of weak acids, such as H_2S, H_3BO_3, CO_2, HNO_2, SO_2, phosphorous acids, and NH_3) dissociate in such a manner that when one calculates the "constant" for each dilution,[2] it is found that the resulting numbers scarcely remain even of the same order of magnitude.

Thus, taking the case of NH_4Cl at 18° C., which we have already cited, a calculation of the "constant" gives the following values for "K":—

NH_4Cl.

v.	Λ.	α.	Ostwald, "K."
1	90·7	0·750	2·2
2	94·8	0·784	1·4
10	103·5	0·856	0·51
20	107·8	0·892	0·37
100	114·2	0·945	0·16
500	118·0	0·976	0·08
1,000	119·0	0·985	0·065
5,000	120·4 Λ_∞	1·000	—
10,000	120·9	"	—
50,000	120·9	"	—

The "constant" increases rapidly as the concentration increases. If, therefore, we assume that the law is obeyed at very great dilution (*i.e.* when $v = 1000$), we could conclude

---

[1] For further instances of acids see Abegg's *Electrolytic Dissociation Theory*.

[2] "α" being calculated from conductivity data.

that undissociated C_6H_5OH is formed, thereby using up $H^{\cdot}$ and C_6H_5O' simultaneously, until the expression—

$$\frac{[H^{\cdot}] \times [C_6H_5O']}{[C_6H_5OH]}$$

has attained the necessary value. But the disappearance of $H^{\cdot}$ necessarily means the further production of OH' ions from the water, since the product of $[H^{\cdot}]$ $[OH']$ is constant, and hence the solution as a whole reacts *alkaline*—alkalinity being due to excess OH'. This is the mechanism based on the theory of electrolytic dissociation to account for the alkalinity of solutions of sodium phenate. The same behaviour is exhibited by sodium carbonate or KCN solutions, because CO_2 and HCN are extremely weak acids. In the case in which we deal with a solution of a salt containing a weak base—say, aniline hydrochloride, or $AlCl_3$—the resultant reaction is acid, for here the OH' of the water is used up in combining with the $Al^{\cdot\cdot\cdot}$ ions to give some undissociated $Al(OH)_3$, which is so weak a base, *i.e.* possesses so small a dissociation constant, that the product of the $Al^{\cdot\cdot\cdot}$ ions and OH' ions in the present case would exceed the necessary value for equilibrium, and since $[H^{\cdot}] \times [OH']$ is always constant, it follows that more $H^{\cdot}$ is produced from the water, as OH' is used up to form $Al(OH)_3$, and $H^{\cdot}$ remains in the solution as such, thereby giving the acid reaction. A very interesting case now presents itself, viz. a solution of a salt made up of two extremely weak components, *e.g.* aluminium acetate, aniline acetate, or ammonium acetate. In this case $H^{\cdot}$ ion is removed from the solution along with acetanion to give some undissociated CH_3COOH. Simultaneously OH' is removed from the solution along with NH_4 or $Al^{\cdot\cdot\cdot}$, to give undissociated NH_4OH or $Al(OH)_3$, and therefore, although the extent of the hydrolysis is very great, the solution is not so acid or so alkaline as in the previous cases. In fact, *if the dissociation constants of the acid and the base were identical, we would have hydrolysis, and yet the solution would be neutral.* The student must therefore be on his guard against assuming that absence of neutrality means absence of hydrolysis. This case, however, is extremely rare;

CASE I.—Let us take the case of a salt consisting of a *strong acid* and *weak base* or *vice versâ.* The reaction is either

$$AB + H_2O = \underset{\text{Practically undissociated.}}{BOH} + \underset{\text{Largely dissociated.}}{HA}$$

or

$$AB + H_2O = \underset{\text{Largely dissociated.}}{BOH} + \underset{\text{Practically undissociated.}}{HA}$$

At equilibrium applying the law of mass action, we obtain—

$$\frac{[BOH] \times [HA]}{[AB] \times [H_2O]} = \text{constant}$$

and since $[H_2O]$ is constant,

$$\frac{[BOH] \times [HA]}{[AB]} = \text{a constant called the } \textit{hydrolytic constant.}$$

Suppose we have dissolved 1 mole of salt AB in v liters of water and x is the fraction hydrolysed, then—

$$\frac{x^2}{v^2} \cdot \frac{v}{1 - x} \quad \text{or} \quad \frac{x^2}{(1 - x)v} = \text{constant}$$

so that as v increases so must x, i.e. *the hydrolysis increases with the dilution.*[1] When the hydrolysis is small $1 - x = 1$ approximately, and x is then $\propto \sqrt{\text{dilution}}$.

ILLUSTRATION.—HYDROLYSIS OF POTASSIUM CYANIDE, KCN (Shields, 1893).

Concentration of KCN in moles per liter $= \frac{1}{v}$.	Fraction of each mole of KCN hydrolysed, *i.e.* concentration of HCN (which is practically undissociated).	$\frac{x^2}{(1-x)v}$.
0·947	0·0031 or 0·31 per cent.	0·9 × 10^{-5}
0·235	0·0072 or 0·72 „	1·22 × 10^{-5}
0·095	0·0112 or 1·12 „	1·16 × 10^{-5}
0·024	0·0234 or 2·34 „	1·3 × 10^{-5}
		Mean 1·1 × 10^{-5}

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[1] It must be observed that this is not always true (see Case II.). The only sound treatment is to consider the effect from the standpoint of ions.

In the cases in which $\frac{K_w}{k_a}$ is small compared with unity, *i.e.* when k_a is considerably larger than K_w, the expression reduces to

$$x = \sqrt{\frac{vK_w}{k_a}} \quad i.e.\ x \propto \sqrt{v} \text{ as before}$$

The hydrolysis of a salt consisting of *one* weak constituent can be calculated if we know the ionic product of water and the dissociation constant of the weak-constituent.

Case II.—Now consider the hydrolysis of a salt containing *both* a weak acid and weak base, *e.g.* urea acetate or aniline acetate. If we start with 1 mole of the salt in v liters, and a fraction x is hydrolysed, then the equilibrium corresponds to $\frac{1-x}{v}$ moles of salt practically completely dissociated,

$$i.e.\ \frac{1-x}{v} = \text{the concentration of } A' \text{ or } B^{\cdot}$$

likewise there are $\frac{x}{v}$ moles acid very slightly dissociated

and $\frac{x}{v}$ „ base „ „

We must take into account the dissociation constants k_a and k_b of the free acid and base. From the dissociation of water we have the relationship

$$[H^{\cdot}][OH'] = K_w$$

For the acid
$$\frac{[H^{\cdot}][A']}{[HA]} = k_a$$

For the base
$$\frac{[B^{\cdot}][OH']}{[BOH]} = k_b$$

Since the dissociation of the acid and base is very small, we may put the concentration of the undissociated acid, viz.

$$[HA] = \frac{x}{v}, \text{ and similarly, } [BOH] = \frac{x}{v}$$

Hence
$$k_a = \frac{[H^{\cdot}]\left[\frac{1-x}{v}\right]}{\frac{x}{v}}$$

second or even third stage hydrolysis coming in, as in the above case, viz.—

$$AlCl_3 + H_2O \rightarrow AlCl_2OH + HCl \text{ first stage}$$
$$AlCl_2OH + H_2O \rightarrow AlCl(OH)_2 + HCl \text{ second stage}$$
$$AlCl(OH)_2 + H_2O \rightarrow Al(OH)_3 + HCl \text{ third stage}$$

Ley carried out a similar series of experiments with many other metallic salts.

The determination of hydrolysis of salts by means of the catalytic saponification of the methyl acetate by means of H˙ ions follows exactly the same general principle as the above. One may also mention the extremely delicate catalytic reaction, viz. the decomposition of diazoacetic ester by means of H˙ ions (Bredig and Fraenkel, *Zeitsch. Elektrochem.*, 11, 525, 1905), whereby [H˙] down to $\frac{N}{1000}$ are determinable, but the presence of neutral salts has a disturbing effect.

The following table (taken from a report by R. C. Farmer, *British Association Report*, 240, 1901) contains the values of the percentage hydrolysis of certain salts at decinormal concentration at 25° C.:—

TABLE.

HYDROLYSIS OF HYDROCHLORIDES OF WEAK BASES as measured by the catalytic decomposition of esters.

Base.	% Hydrolysis.	Base.	% Hydrolysis.
Glycocoll . . .	19	Urea	90
Asparagine . .	25	Acetamide . .	98
Acetoxime . . .	36	Thiourea . . .	99

HYDROLYSIS OF ALKALI SALTS OF WEAK ACIDS as measured by the catalytic saponification of esters.

Acid.	% Hydrolysis.	Acid.	% Hydrolysis.
Hydrocyanic . .	1·12	p. chlorophenol .	1·62
Acetic	0·008	p. cyanphenol .	0·29
Carbonic . . .	3·17	p. nitrophenol .	0·16
Phenol	3·05		

infinite dilution,[1] as equal to 383 at 25°. Λ_v stands for the equivalent conductivity the salt *would* have possessed had no hydrolysis taken place.

This can be evaluated by the method of Bredig (*Zeitsch. physik. Chem.*, **13**, 214, 1894), namely, by the addition of a sufficiently great excess of the free base to the hydrolytic salt solution until we reach the condition that—

$$\Lambda = \Lambda_v, \text{ i.e. } x = 0$$

which must be obtained when the Λ *observed has become independent of the quantity of free base added.* The applicability of this method obviously depends on the validity of assuming that the conductivity of the base itself is negligibly small compared with that of the salt. The following data are given by Bredig (*l.c.*) for the hydrolysis of aniline hydrochloride :—

The column headed Λ denotes the values of the equivalent conductivity when the solution is diluted with water only.

The column marked $\Lambda_v(32)$ denotes equivalent conductivity with $\frac{N}{32}$ aniline present in the solution.

The column marked Λ_v64 denotes values obtained with $\frac{N}{64}$ aniline present.

v.	Λ.	Λ_v32.	Λ_v64.
64	106·2	95·9	96·0
128	113·7	98·1	98·2
256	122·0	100·1	100·3
512	131·8	101·4	101·5
1024	144·0	103·3	103·3

The agreement between the two final columns shows that even with $\frac{N}{64}$ aniline present the hydrolysis of the salt has practically disappeared, for on increasing the aniline to

---

[1] Strictly the HCl will not be in general completely dissociated, but no very serious numerical error is thereby introduced.

say about 95 per cent., is changed over into the form of ions. Now this change, or neutralisation, of the indicator does actually require a certain definite amount of alkali for its completion, and the more indicator is present the more alkali will be needed. Most indicators of this class are, however, used in such dilute solution that this effect is negligible; and it is further important to notice that even if the concentration of the indicator is moderately high, the accuracy of the titration will not be affected if the indicator is originally put into the solution in the same form as it will have at the end of the titration. From this point of view, such indicators as methyl orange, methyl red, nitrophenol, must be used in the form of their sodium or potassium salts.

"Bearing all these facts in mind it is possible to draw up a table showing the 'end-points' of various indicators when used in the ordinary manner in titration. Thus we have already seen that the colour change of methyl red is only complete when the concentration of hydrogen ions is something less than 10^{-6}; and the end-point observed when methyl red is used as an indicator in the ordinary manner lies somewhere between $10^{-5.7}$ and $10^{-6.4}$, the variation being relatively unimportant, and due to the inability of the eye to detect small changes in colour without a special apparatus. The following table gives the values of the end-points of the more common indicators; the actual numbers are probably not extremely accurate in some cases, but our knowledge is at present too imperfect to allow of their being defined with greater precision:—

Methyl orange	$10^{-4.5}$ to $10^{-5.5}$
Methyl red	$10^{-5.7}$ to $10^{-6.4}$
Litmus	$10^{-6.5}$ to $10^{-7.5}$
Phenolphthaleïn	$10^{-8.2}$ to 10^{-9}
Thymolphthaleïn	$10^{-10.5}$ to $10^{-11.5}$

"Having arrived at these numbers, all that remains is to consider how the concentration of hydrogen ions changes in a solution when we titrate acids and bases of various strengths. When we know this, we can not only decide upon the

and since $$ac = k_a u$$

$$c = \frac{k_a u}{a}$$

Further, since $$bd = k_b u$$

$$d = \frac{k_b u}{b} = \frac{k_b u_a}{K}$$

Now consider the special case of an amphoteric electrolyte whose basic dissociation constant $k_b =$ the acidic dissociation constant k_a.

As before— $$ac = k_a u$$

$$bd = k_b u$$

and since $$k_a = k_b$$

it follows that $$ac = bd$$

$$\therefore \frac{b+c}{b} = \frac{a+d}{a}$$

Also, since the solution is electrically neutral, it follows that—

$$a + d = b + c$$

$$\therefore a = b \quad \textit{i.e.} \quad [\text{H}^{\cdot}] = [\text{OH}']$$

and $$c = d \quad [\text{XOH}'] = [\text{XH}^{\cdot}]$$

The solution is therefore chemically neutral at all dilutions, since

$$\text{OH}' = \text{H}^{\cdot} = 10^{-7} \text{ gram-equiv. per liter.}$$

Again, $$c = \frac{k_a u}{a} \qquad d = \frac{k_b u}{b} = \frac{k_b a u}{K}$$

$$\therefore c + d = \frac{k_a u}{a} + \frac{k_a a u}{K}$$

$$\therefore \frac{c+d}{u} = k_a\left[\frac{1}{a} + \frac{a}{K_w}\right]$$

Now a has been shown to be constant at all dilutions.

Hence— $$\frac{c+d}{u}$$

is constant at all dilutions, *i.e.* the degree of dissociation of the amphoteric body is independent of the dilution.

Take as an example a substance with dissociation constants $k_a = k_b = 1 \cdot 2 \times 10^{-7}$ (at 25° C.).

form of Ostwald's dilution law to the electrolytic dissociation of water itself, namely—

$$H_2O \rightleftarrows H^{\cdot} + OH'$$

the equation taking the form—

$$\frac{C_{H^{\cdot}} \times C_{OH'}}{C_{H_2O}} = \text{constant}$$

or, since the concentration of the water is constant, $C_{H^{\cdot}} \times C_{OH'} = \text{constant}$. This constant may be called the "ionic product" as well as ionisation constant. In the case of saturated solutions of electrolytes in which some solid is present, the idea of distribution, as we have seen, would lead to an equilibrium being set up when there is equality in the number of molecules passing in opposite directions to and from the solid. The ratio of the concentration in the two phases is constant at the equilibrium point by definition, and since the "concentration" in the solid is constant, the concentration of molecules in solution is constant as long as we can regard the solvent as the same, *i.e.* as long as it is unmodified by the presence of the ions themselves. It will be noted that we are dealing with the distribution of the same kind of molecular species as is necessary in accordance with Nernst's definition of the distribution law.

Now let us consider the application of the law of mass action to the dissolved state, *i.e.* the ions and molecules. If we are dealing with a simple binary dissociation such as that of AgCl into $Ag^{\cdot}$ and Cl', we have the relation—

$$\frac{[Ag^{\cdot}][Cl']}{[AgCl]} = \text{constant}$$

supposing the simple form of the law of mass action, *i.e.* the dilution law, to hold good. But we have just seen that in the saturated state [AgCl] is constant—

$$\therefore\ [Ag^{\cdot}][Cl'] = \text{a constant}$$

called the SOLUBILITY PRODUCT OF IONIC PRODUCT. This is of fundamental importance in dealing with solubility relations of electrolytes especially of sparingly soluble salts. It will be seen from the above that if we increase the concentration

WATER AS MEDIUM.

The last three substances were the least stable, being precipitated from solution in a week.

ETHYL ALCOHOL AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt per cm.
Pb, Sn, Zn } Hydroxides probably.	(+) (+) (+)	$4·5 \times 10^{-5}$ 3·6 2·8

Ag, Au, Pt, Bi, Fe, Cu could not be prepared in the form of stable solutions in ethyl alcohol.

METHYL ALCOHOL AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt per cm.
Pb	(+)	22×10^{-5}
Bi	(+)	10·2

ETHYL MALONATE AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt. per cm.
Pt	(−)	$2·3 \times 10^{-6}$
Ag	(−)	1·7
Au	(−)	1·4

that when colloidal arsenic sulphide (negatively charged) was precipitated by $BaCl_2$ this salt was partly decomposed, a small quantity of $Ba(OH)_2$ being found in the precipitate, which could not be washed out completely, even after prolonged trial, and simultaneously a little free HCl was found in the supernatant liquid. This close union, which in the above instance exists, between the barium ion (in the form of baryta) and the coagulated colloid, is found frequently in the case of other ions in physiological liquids containing organic colloids. Reference has already been made to an analogous phenomenon in dealing with the osmotic pressure of certain physiological colloids and dyestuffs.

Coagulation of a colloid is in certain cases a reversible phenomenon, though it is more frequently irreversible. Besides being brought about by the addition of electrolytes, it may also be caused by heating or cooling the colloidal solution as well as by electrolysis (more correctly speaking by cataphoresis), the particles being carried in virtue of their charges to one of the electrodes, where they become discharged and assume the gel form. (Reversible coagulation is only met with in certain cases, *e.g.* gelatine, when the coagulation has been brought about by temperature changes. It is never found when coagulation is brought about by addition of electrolytes.)

A very remarkable phenomenon in connection with coagulation is the *protective action* of other colloids also present in the solution. Thus colloidal platinum is rendered much less sensitive to coagulating agents by the addition of a little gelatine to the solution. The mechanism of the process is at present unknown.

It should be remembered that the colloidal state plays a greater *rôle* in ordinary chemical operations and reactions than is generally supposed. From the peculiar form in which substances (simple inorganic bodies) may be precipitated under certain conditions, it seems not unlikely that the colloidal state (sol and gel) represents at least a transition stage in such phenomena. Thus it is possible to precipitate barium sulphate (which is ordinarily a definitely crystalline substance) in a form not very different from a thin jelly, which passes over more or less rapidly into the stable form. Further, in the electrolytic precipitation of metals, such as copper, the formation of a smooth deposit is assisted by the presence of a little gelatine in the bath—an effect which reminds one of the "protective action" mentioned above. This effect in the case off copper electrolysis has, however, been called recently in question. The coagulation phenomena observed in the case of colloids has also been observed in the case of suspensions and emulsions, though these have been less extensively investigated (*cf.* Bodländer, *Jahrbuch für Mineralogie*, **2**, 147, 1893).

We are now in a position to return to the question of the electrical charge on a colloidal particle as determined by Burton (*l.c.*) from the amount of $Al_2(SO_4)_3$ just required to cause precipitation. Burton determined this by measuring the velocity of the colloid particle in an electric field when different amounts of electrolyte were present. The following data were obtained for colloidal silver in water :—

6·5 MILLIGRAMS SILVER PER 100 C.C. SOLUTION.

Grams of $Al^{\cdot\cdot\cdot}$ [1] per 100 c.c. solution.	Specific conductivity of the solution at 18° C.	Velocity of silver sol in cm. per second under 1 volt per cm. gradient.
0	$31{\cdot}0 \times 10^{-6}$	$22{\cdot}4 \times 10^{-5}$ towards anode
14×10^{-6}	$30{\cdot}3 \times 10^{-6}$	$7{\cdot}2 \times 10^{-5}$,, ,,
38×10^{-6}	$29{\cdot}7 \times 10^{-6}$	$5{\cdot}9 \times 10^{-5}$,, cathode
77×10^{-6}	$28{\cdot}5 \times 10^{-6}$	$13{\cdot}8 \times 10^{-5}$,, ,,

The colloid, which by itself is negatively charged, becomes eventually positively charged on addition of $Al_2(SO_4)_3$, and at the region in which the $Al^{\cdot\cdot\cdot}$ is 26×10^{-6} grams per 100 c.c. the velocity would be zero. This is called the *isoelectric point* (Hardy), and at this point the critical concentration of $Al^{\cdot\cdot\cdot}$ is reached for coagulation. As a matter of fact, the colloid which travelled towards the cathode was very unstable, and precipitated itself after a short time. The velocity method is the most exact method for determining the coagulating point, *i.e.* the "critical" amount of electrolyte required.

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[1] No allowance was made for hydrolysis of $Al_2(SO_4)_3$ giving rise to $Al(OH)_3$, which is very slightly dissociated.

$$\therefore \frac{1}{t} \log \frac{\frac{Ka}{K-1}}{\frac{Ka}{K-1} - x} = k_1 - k_2$$

or

$$k_1 + k_2 = \frac{1}{t} \log \frac{Ka}{Ka - (K + 1)x}$$

This expression was verified by Henry as follows:—

K was found at 25° C. = 2·68

t minutes.	x.	Value of $\frac{1}{t} \log \frac{Ka}{Ka - (K+1)x}$
21	2·39	0·0411
50	4·98	0·0408
80	7·14	0·0444
120	8·58	0·0400
220	11·56	0·0404
320	12·57	0·0398
47 hours (equilibrium reached)	13·28 (used for K calculation)	—

Another example of monomolecular opposed reactions is to be found, in adding a small quantity of acetic acid to a concentrated solution of water and alcohol, whereby, of course, ethyl acetate is formed, but the alcohol and water concentration may be regarded as constant, so that the reaction is virtually acid ⇄ ester, and the equation is—

$$\frac{dx}{dt} = k(a - x) - k'x_2$$

where a is the amount of acid present initially, and x is the amount transformed into ester.

The same reaction, as already pointed out, is bimolecular, when no component is present in excess. Thus, if one mole of ester + one mole of water are present to start with, then at time t

$$\frac{dx}{dt} = k_1(1 - x)^2 - k_2x^2$$

and $\frac{k_1}{k_2} = \frac{1}{4}$ (Berthelot and Pean de St. Gilles)

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